Res Chem Intermed
DOI 10.1007/s11164-010-0190-x

Microstructure of $NiTiO_3$–TiO_2 eutectic and its magnetic properties

Do Nam Binh · Park Sang In · Luu Van Tho

Received: 1 February 2010 / Accepted: 16 April 2010

Abstract The growth of $NiTiO_3$–TiO_2 eutectic by the micro-pulling-down method was studied. According to the phase diagram, the eutectic composition is at 63.36 mol % TiO_2 and 36.64 mol % NiO at 1,570 °C. The preliminary results on the crystal growth and the microstructure composite structure-like laminate of the eutectic is presented. The dependence of the microstructure refinement on the pulling rate is also presented, as well as the preliminary results on magnetic properties.

Keywords Eutectics · Micro-pulling-down method · Crystal growth · Microstructure · Magnetic properties of eutectic

Introduction

Metal–metal eutectics have been studied for many years because of their excellent mechanical properties. Recently, oxide–oxide eutectics have also been studied for their excellent flexural strength and creep resistance at high temperature [1–3]. Experimental data for oxide–oxide eutectics or hybrid eutectics such as metal–oxide and semiconductor–oxide are still very limited. Oxide–oxide eutectics were recently studied as optical materials [4, 5] and proposed as materials that could act as photonic crystals [6–8]. Depending on different factors, such as the entropy of melting of both phases, eutectics can form different microstructures and nanostructures, classified by Hunt and Jackson [9] as nonfaceted–nonfaceted, nonfaceted–faceted, and faceted–faceted. The eutectic microstructure can exhibit

D. N. Binh · P. S. In · L. Van Tho
Department of Materials Science and Engineering, Chungnam National University, Daeduk Science Town, Daejeon 305-764, Korea

L. Van Tho (✉)
School of Material Science and Engineering, University of Ulsan, Ulsan 680-749, Korea
e-mail: tholuuvan@yahoo.com; t.v.luu@fys.uio.no

Published online: 16 September 2010

many geometrical forms. It can be regular-lamellar, regular-fibrous, irregular, complex regular, quasiregular, broken-lamellar, spiral, or globular. The most interesting from the point of view of photonic crystals would be microstructures with regular shapes, i.e., lamellar and fibrous shapes, whereas for metamaterials [10, 11] applications, other possible shapes would also be of interest, e.g., percolated structures for giant dielectric constant [12, 13] or spiral for chiral metamaterials. A globular shape might also find application in invisible materials [14] or in plasmon-tunable materials if the structure was metallodielectric [15].

The primary aim of this paper is to present the experimental results on the growth of the eutectic with the first composition **$NiTiO_3$–TiO_2**; the eutectic microstructure; and its magnetic properties.

A secondary aim of this paper was to study a new eutectic composition while looking for a eutectic with an interesting microstructure. This is because self-organized oxide–oxide eutectic structures have a potential for application in the field of magnetics.

Experimental section

Crystal growth

The micro-pulling-down method was invented in Japan originally for the growth of single-crystal fibers [16, 17]. The growth of oxide–oxide eutectics for high-strength materials has already been presented by this method [18, 19]. The micro-pulling-down method utilizes a crucible with a die at the bottom in which there is a centrally placed nozzle. The raw materials are melted in the crucible; the melt that exudes from the nozzle is touched with the seed crystal, and the crystal is pulled down. The details of the thermal system we used for micro-pulling-down, as well as the growth conditions, are described elsewhere [20]. The crystals were seeded grown with a $YAlO_3$ single crystal. High-purity oxide powders (99.995%) NiO and TiO_2 were used as starting materials. The oxides were mixed with ethanol in an alumina mortar and then dried.

X-ray diffraction

X-ray powder diffraction measurements were performed on the as-grown, annealed, and demolished samples using a Siemens D500 diffractometer equipped with semiconductor Si:Li detector and Cu K_α radiation. The powder diffraction pattern was measured in a õ/2õ scanning mode with a step of 0.02° and counting time of 10 s/step. The experimental data were analyzed by the Rietveld refinement using the DBWS-9807 program package of Young. The orientation of the eutectic was examined using a four-circle KUMA-diffraction KM4 diffractometer and Cu K_α radiation.

Quantitative analysis of the microstructure

All the geometrical parameters were calculated from the scanning electron microscope images by the MICROMETER program.

Magnetic measurements

The magnetic properties were measured with a DMS vibrating sample magnetometer (VSM) and a SHB-109 BH loop tracer. The effective permeability of the thin films was measured in the range of 1–3,000 MHz by network analyzer HP4191A.

Results and discussion

In this work, the eutectic with a composition of 63.36% TiO_2 and 36.64% NiO was grown by the micro-pulling-down method with different pulling rates (p.r.): 0.15, 0.45, 1, and 5 mm/min. The as-grown crystal has a gray coloration (Fig. 1).

The powder XRD confirms the presence of two phases in the as-grown eutectic (Fig. 2). The first one is perovskite structure, $NiTiO_3$, which crystallizes in the rhombohedric system in the *R*3c space group, with the lattice constants: (a) 5.332 Å, (c) 12.97 Å. The diffraction peaks of the second phase are most closely matched by the diffraction pattern of TiO_2. The available databases did not contain any diffraction data for hexaluminate, $NiTiO_3$<220>.

The poly-crystal XRD from the plane of the eutectic rod perpendicular to the growth direction reveals that the $NiTiO_3$ crystal appears to grow in

Fig. 1 The gray $NiTiO_3$–TiO_2 eutectic rod

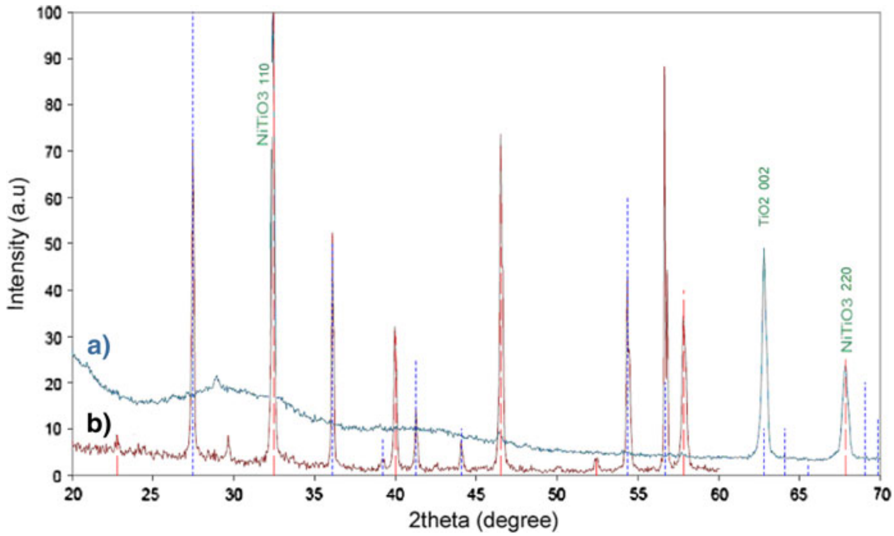

Fig. 2 X-ray diffraction pattern: (*a*) powder measurement—*black line*, (*b*) single crystal of as-grown $NiTiO_3$–TiO_2 eutectic

the <110> direction. Although there is also a trace of the <220> orientation, as indicated by the presence of an <220> reflection at $2\theta = 67.5°$. For the TiO_2 phase, all the reflections seem to be present in the single-crystal diffraction pattern, with a slightly preferred direction of growth being <002>. In the eutectics we have investigated until now, it was always a matrix that grew in the whole rod in one crystallographic direction. Evidently, because of some disturbances in growth leading to a microstructure which is not completely homogeneous, the phase forming the pattern does not show one totally distinguished direction in the whole of the eutectic rod. However, in some large regions that do have a homogeneous structure, such a direction has been distinguished using the electron back-scattering diffraction method.

The $NiTiO_3$–TiO_2 eutectic tends to grow with a fibrous/rodlike microstructure, with the $NiTiO_3$ microfibers packed in the matrix of TiO_2. The diameter of $NiTiO_3$ microfibers can be controlled by the pulling rate. With p.r. = 3 mm/min, the average diameter of microfibers/microrods is 5–7 nm (Fig. 3). In Fig. 4, the change of the microstructure size of eutectics grown with different pulling rates: 0.15, 0.45,

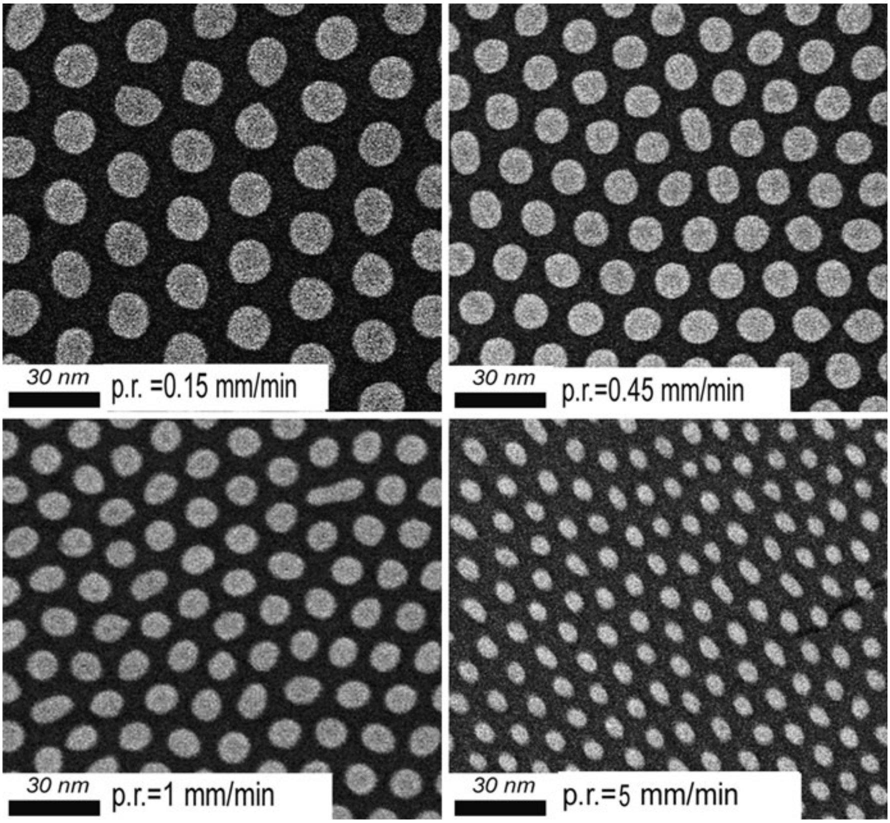

Fig. 3 The change of the microstructure size of the binary eutectic $NiTiO_3$–TiO_2 when it is grown with different pulling rates

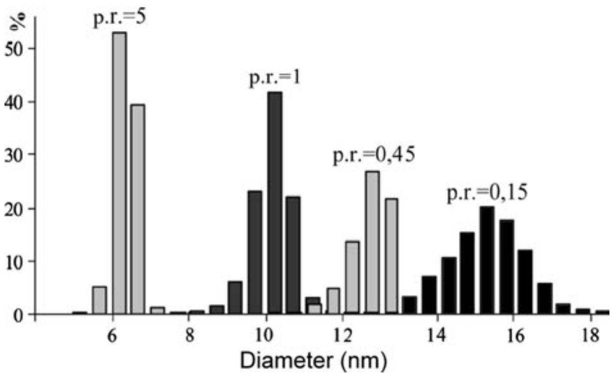

Fig. 4 Microrod diameter distribution for eutectics grown with different pulling rates (*p.r.*) indicated above the histograms

1, and 5 mm/min are shown. The eutectic microstructure decreases with increasing p.r. In addition, the microstructure is more regular with a more circular cross-section of the microrods with an increase of the pulling rate. For the eutectics grown with a small p.r. of 0.15 mm/min, the microfibers cross-section is not very circular. This improves when increasing the p.r. The longitudinal section of the eutectics (parallel to the crystal growth direction) is shown in Fig. 4, which shows the microfibers. In almost all cases, short pieces of microfibers are seen in longitudinal section; long, straight microfibers are rarely found. One explanation is that the microfibers probably tend to be sinusoidally shaped, or the eutectic rod is not cut parallel to the growth direction.

The quantitative description of the microstructures has been performed using the MICROMETER 0.99b program. All the parameters for each eutectic were calculated from a few SEM micrographs. The summary files contained from 736 to 6,038 data points (microrods). Then the average parameters were calculated. In the areas investigated, all the parameters are very similar to each other, as demonstrated by the coefficient of variation (CV), which is almost always very close to zero. The mean equivalent diameter, $d2$, of the microrods changes from 3.87 to 18.39 nm for pulling rates of 0.15 and 5 mm/min, respectively. The distribution of the microrod diameter of eutectics grown with different pulling rates is shown in Fig. 4.

The hysteresis loops for an applied magnetic field in the hard axis of films after cutting for 2 mm thickness at different pulling rates from 0.15 to 5 mm/min are shown in Fig. 5. There is a strong variation in the shape of the hysteresis curve. With increasing pulling rate, the magnetic saturation and the anisotropy magnetization decrease quickly from 15.5 kG and 55 Oe to 13 kG and 30 Oe, respectively. This phenomena show that pulling rate strongly influenced the change of the magnetic saturation and the anisotropy magnetic of the film. When pulling rate increase, the ratio of volume of $NiTiO_3/TiO_2$ decrease and then the magnetic saturation decrease. Since the grains are expected to be oriented randomly, the origin of the observed anisotropy in thin films has also been observed in crystalline [21], and therefore, is expected to be related to anisotropic ejection of the pulling

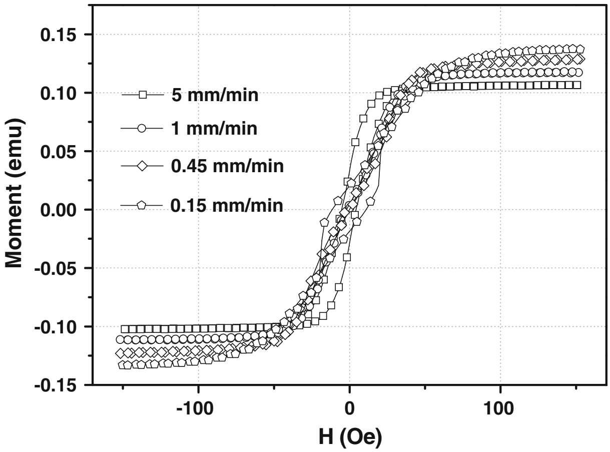

Fig. 5 The sharp of hysteresis loops under difference of pulling rate, as the effect of pulling rate on the magnetic saturation and magnetic anisotropy

directiond. Figure 5 also displays the pulling rate dependence of pining coercive. The coercivity value decreases quickly along with the increase of pulling rate. The observed behavior may be attributed to a combined effect of the increase in surface roughness and the decrease in internal stresses as evidenced from a rapid decrease in the magnetic anisotropy.

Conclusion

A new eutectic with the composition of 63.36% TiO_2 and 36.64% NiO has been grown, and its structural and spectroscopic properties have been studied. Powder XRD confirms the presence of only two phases, $NiTiO_3$<220> and TiO_2<002>. The NiO–TiO_2 eutectic tends to grow with a fibrous microstructure, with the $NiTiO_3$<110> phase forming microrods packed pseudohexagonally in the TiO_2 matrix. The eutectic has been grown with different p.r.: 0.15, 0.45, 1, and 5 mm/min. The smallest microrods grown with p.r. = 5 mm/min were 300 nm in diameter. Applying higher pulling rates resulted in more regular microrods. This fibrous/rodlike microstructure may have a potential for application in modern photonics in the field of photonic crystals and/or metamaterials. The pulling rate strongly influenced the change of the magnetic saturation and the anisotropy magnetic of the film. When pulling rate increased, the magnetic saturation and magnetic anisotropy decreased while the coercivity increased. This method is a strong candidate for magnetic device fabrication in the future.

Acknowledgment The authors thank the Ministry of Scientific Research and Information Technology of Poland for support of this work (Grant No. 4 T11B 015 24). The authors acknowledge the Network of Excellence, METAMORPHOSE (No. 500252), and also thank Dr. Siân Howard (University of South Australia) for a critical reading of the manuscript.

References

1. Y. Waku, N. Nakagawa, T. Wakamoto, H. Ohtsubo, K. Shimizu, Y. Kohtoku, Nature **389**, 49 (1997)
2. J.H. Lee, A. Yoshikawa, H. Kaiden, K. Lebbou, T. Fukuda, D.H. Yoon, Y. Waku, J. Cryst. Growth **231**, 179 (2001)
3. J. Llorca, V.M. Orera, Prog. Mater. Sci. **51**, 711 (2006)
4. R.I. Merino, Phys. Rev. **B 56**, 10907 (1997)
5. V.M. Orera, Appl. Phys. Lett. **71**, 2746 (1997)
6. D.A. Pawlak, G. Lerondel, I. Dmytruk, Y. Kagamitani, S. Durbin, T. Fukuda, J. Appl. Phys. **91**, 9731 (2002)
7. R.I. Merino, J.I. Pena, A. Larrea, G.F. de la Fuente, V.M. Orera, Recent Res. Dev. Mater. Sci. **4**, 1 (2003)
8. D.W. Bahnemann, J. Res. Chem. Intermed. **26**, 2 (2000)
9. J.D. Hunt, K.A. Jackson, Trans. AIME **236**, 843 (1966)
10. J.B. Pendry, Phys. Rev. Lett. **85**, 3966 (2000)
11. R. Shelby, D.R. Smith, S. Schultz, Science **292**, 77 (2001)
12. C. Pecharroman, F. Esteban-Betegon, J.F. Bartolome, S. Lopez-Esteban, J.S. Moya, Adv. Mater. **13**, 1541 (2001)
13. J.K.S. Wan, I. Kalatchev, J. Dziak, M. Catherine Depew, J. Res. Chem. Intermed. **27**(9), 917 (2001)
14. F.J. Garcia de Abajo, G. Gomez-Santos, L.A. Blanco, A.G. Borisov, S.V. Shabanov, Phys. Rev. Lett. **95**, 067403 (2005)
15. S. Riikonen, I. Romero, F.J. Garcia de Abajo, Phys. Rev. **B71**, 235104 (2005)
16. D.H. Yoon, I. Yonenaga, N. Ohnishi, T. Fukuda, J. Cryst. Growth **142**, 339 (1994)
17. P. Rudolf, T. Fukuda, Cryst. Res. Technol. **34**, 3 (1999)
18. J.H. Lee, A. Yoshikawa, S.D. Durbin, D.H. Yoon, T. Fukuda, Y. Waku, J. Cryst. Growth **222**, 791 (2001)
19. J.H. Lee, A. Yoshikawa, H. Kaiden, K. Lebbou, T. Fukuda, D.H. Yoon, Y. Waku, J. Cryst. Growth **231**, 179 (2001)
20. K. Kolodziejak, S. Turczynski, R. Diduszko, L. Klimek, D.A. Pawlak, Optoelectron. Rev. **14**, 203 (2006)
21. M. Li, Y.P. Zhao, G.C. Wang, H.G. Min, J. Appl. Phys. **83**, 5313 (1998)